Electrolytes near a charged surface: Integral equation approximations (Grant Goodyear, Andrew C. Eaton, Michael J. Booth, and Anthony D. J. Haymet [University of Houston])

We are currently developing the code required to study the equilibrium structure of various electrolytes — our current projects include dissolved salts, molten salts, and autoionizable water — in the presence of an electrode. Along with electrolyte structure, we will also calculate charge profiles, the mean electrostatic potential, and the double-layer capacitance. Our initial focus is on simple 2-2 electrolytes or molten KCl near an infinite planar electrode, but the same methodology applies to the much more exotic cases, such as that of water structure (and pH) near an arbitrarily shaped electrode such as a strand of DNA or a protein.

In principle, "all" we have to do is solve the following inhomogeneous Ornstein-Zernike equation:

$$[g_{ss'}(\vec{r}_1, \vec{r}_2) - 1] = c_{ss'}(\vec{r}_1, \vec{r}_2) + \sum_{s''} \int d\vec{r}_3 \, \rho_{s''}(\vec{r}_3) \, c_{ss''}(\vec{r}_1, \vec{r}_3) \, [g_{s''s'}(\vec{r}_3, \vec{r}_2) - 1] \qquad (1)$$

where $g_{ss'}(\vec{r}_1, \vec{r}_2)$ is the species *s*-species *s'* radial distribution function and $c_{ss'}(\vec{r}_1, \vec{r}_2)$ is the associated direct correlation function, along with associated density

$$\rho_{s''}(\vec{r}_3) = \rho_{s''}[\{g_{ss'}\}, \{c_{ss'}\}, \vec{r}_3] \qquad (2)$$

and "closure"

$$c_{ss'}(\vec{r}_1, \vec{r}_2) = c_{ss'}[\{\rho_s\}, \{g_{ss'}\}, \vec{r}_1, \vec{r}_2] \qquad (2)$$

relations.

There are several complications, however. Although exact density relations [Eq. (2)] exist, there are only approximate closure relations [Eq. (3)] available; we will want to try several. Long-range forces prevent a naïve implementation of Eq. (1) from converging, but analytical techniques exist to solve the long-ranged portions of Eq. (1), thereby allowing us to replace Eq. (1) with a short-ranged version. The most significant complication, however, is the fact that Eq. (1), at its most general, comprises six degrees of freedom r1, r2 (in three dimensions). Numerically solving Eq. (1) involves mapping the degrees of freedom onto a grid, and then performing a high-dimensional root search. Using a slightly immodest grid of 100 points for each degree of freedom, six degrees of freedom would correspond to a 10^{12}-dimensional root search. We intend to use EMSL's IBM SP along with an off-the-shelf parallelized non-linear equation solver (such as PETSc, http://www.mcs.anl.gov/petsc, by S. Balay, W. D. Gropp, L. C. McInnes, and B. F. Smith) to satisfy the large computational requirements.